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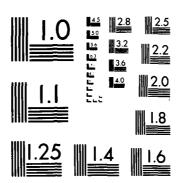
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Proton Abstraction As A Route To Conductive Polymers

bу

Lawrence F. Hancock, Brian L. Hilker, William Chapman and Bernard Gordon III

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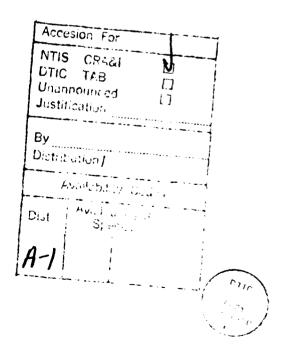
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L. F. Haneock, B. Hilker, W. Chapman and B. Gordon III								
Deaprtment of Materials Science and Engineering, Polymer Science Program The Pennsylvania State University, University Park, PA 16802								
Proton abstraction doping has been demonstrated as a viable alternate procedure for the synthesis of electrically conductive polymers through the preparation of poly(p-								
phenylene pentadienylene), which when doped displayed a conductivity of 10 <sup>-1</sup> S/cm.								
Additional procedures being used for the synthesis of proton abstraction doping								
precursors includes sulfur ylide and Grignard condensations, details will be								
presented. These systems offer tremendous advantages for the study of effects arising from dopant density and conjugation length in organic conductors. One								
interesting result involves the conductivity of 1,5-diphenylpentadiene, a low								
molecular weight model for poly(p-pheynlene pentadienylene). 1.5-Diphenylpentadienyl								
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anion displays a conductdivity of 8S/cm which supports the conclusion that polymeric delocalization of charge is not a necessity.



PROTON ABSTRACTION AS A ROUTE TO CONDUCTING POLYMERS
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Although the structural, electrical, and solid-state properties of conducting polymers have received much attention from researchers', new "doping" methods have not been pursued. This work reports our ongoing research into an alternative synthetic procedure for the preparation of electrically conductive polymers, by proton abstraction "doning".

It can easily be seen that identical charge delocalized systems can be prepared through either reduction of an all-conjugated polymer or through proton abstraction from a polymer whose conjugated sequence lengths are interrupted by relatively acidic methylene moieties, figure 1.

FIGURE 1

Proton abstraction has been confirmed as a viable technique through the synthesis of poly(p-phenylene pentadienylene) and its doping by treatment with n-BuLi. Preliminary electrical measurements for the dark blue/black solid showed a conductivity of  $5.0 \times 10^{-1}$  S/cm.

Many polymeric structures applicable to proton abstraction doping may be proposed. Synthetic routes being pursued in our laboratory include Wittig, sulfur ylide and Grignard condensations. A Wittig procedure was used for the synthesis of poly(p-phenylene pentadienylene) (3), figure 2.

FIGURE 2

Sulfur ylide chemistry has previously been used for the synthesis of poly(phenylene vinylene). A similar procedure is being used for the preparation of poly(methylene-p,p'-stilbenylene) (7), figure 3.

Compound 4, which is prepared through the chloromethylation of diphenylmethane, has also been employed in a bis-Grignard condensation with terephthalaldehyde for the preparation of 10, figure 4. Detailed results will be preparated.

These systems offer tremendous advantages for the study

of effects arising from dopant density and conjugation length in organic conductors. Interesting results with regard to conjugation length have been obtained for the poly(p-phenylene pentadienylene) system.

## FIGURE 4

1,5-Diphenylpentadiene (2), an analogous low molecular weight model, displays a conductivity of 85/cm upon proton abstraction doping to form the 1,5-diphenylpentadienyl anion. This is comparable to conductivity measurements on arene radical cation salts normal to the stack direction of the aromatic rings (1-105/cm). Enhanced conductivities parallel to the stack direction (10 5/cm) suggest that orientation of the most probably amorphous 1,5-diphenyl-pentadienyl anion should lead to enhanced conductivities.

In conclusion, additional synthetic schemes for the preparation of proton abstraction doping precursors are being developed as supplements to the previously developed Wittig procedure. The ability to control the nature and location of the dopant site makes these systems versatile subjects for future studies.

ACKNOWLEDGEMENT: The support of the Office of Naval Research is gratefully acknowledged.

## REFERENCES

- See for instance, "Electronic Properties of Polymers and Related Compounds", H. Kuzmany, H. Mehring and S. Roth, Eds., Springer-Verlag, Berlin (1985).
- B. Gordon III and L. Hancock, <u>Macromolecules</u>, submitted.
- 3) J. Capistran, D. Gagnon, S. Antoun, R. Lenz and F. Karsan, Polym Bran, 25(2), 282 (1984)
- Karasz, Polym. Prep. 25(2), 282 (1984).
   V. Enkelmann, K. Gockelmann, G. Weiners and M. Hokenbusch, Mol. Cryst. Liq. Cryst. 120, 195 (1985).

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